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C. L. McCormick[a]; K. C. Lin[a]
[a] Department of Polymer Science, University of Southern Mississippi, Mississippi

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Water-Soluble Copolymers. II. Synthesis and Characterization of Model Dextran-g-Acrylamides by Ce(IV)/HNO_3-Induced Initiation

CHARLES L. McCORMICK and KAO CHING LIN

Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39401

ABSTRACT

In order to develop polymers useful as mobility control agents in enhanced oil recovery processes, water-soluble acrylamide grafted polysaccharide copolymers have been synthesized in water at 25°C using a ceric ammonium nitrate/nitric acid system. The effects of varying concentrations of ceric ion, monomer, and substrate on conversion, graft length, and molecular structure of the reaction products have been examined. The crude reaction products were purified by fractional precipitation and then were analyzed for nitrogen content using a micro-Kjeldahl method. The chemical structures of the graft copolymers were studied by selective hydrolysis of the carbohydrate backbones. Intrinsic viscosity and grafting length data were used to predict solution behavior of the graft copolymers prepared under controlled conditions. Aqueous size exclusion and viscosity studies showed direct correlations between hydrodynamic volume and length of the polyacrylamide side-chain grafts.

INTRODUCTION

The escalation of crude oil prices and the impending shortage of petroleum has focused attention on economically feasible methods of enhanced oil recovery (EOR). One such method involves the use of polymers as mobility control fluids in displacing residual oil from reservoirs. The many requirements necessary for a candidate polymer to perform adequately in this application have been reviewed [1]. From an economic viewpoint, high solution viscosities (large hydrodynamic volumes) must be maintained at relatively low polymer concentrations. Additionally, the polymer must remain in solution while permeating the porous medium to displace the residual oil without degradation or adsorption.

Our investigations of the possibility of utilizing water-soluble graft copolymers prepared from naturally-occurring polysaccharides continue [2-7]. The objectives of this study were to prepare a series of model dextran-g-acrylamide copolymers under homogeneous conditions using the Ce(IV)/HNO_3 initiation system and to investigate interrelationships between structure and hydrodynamic volume. A further goal was to optimize reaction conditions to eliminate homopolymer formation and to control the number of grafting sites and side-chain graft length. Dextran was chosen as a model polysaccharide since it is available in well-characterized form at varying molecular weights. Acrylamide was chosen as the grafting monomer since its homopolymer (and the partially hydrolyzed version) is widely used in EOR applications.

Graft copolymerization of vinyl monomers onto polysaccharides by Ce(IV) induced initiation is an effective synthetic method due to its simplicity and controllability [9]. The reaction by which Ce(IV) interacts with polysaccharides to form a free radical involves the formation of a coordination complex between Ce(IV) and the hydroxyl groups of the polysaccharides. Bains and Arthur [10, 11] discussed the mechanism of the grafting reaction and reported ESR evidence for the formation of the free radical. Reyes [12] grafted starch with acrylamide at different Ce(IV) concentrations and identified the graft copolymer by infrared spectroscopy coupled with an acid hydrolysis method. Wallace's study [13], which dealt with the kinetics of dextran-g-acrylamide grafting reactions, concluded that the rapid rate of polymerization was due to the high reactivity of the ceric ion with the terminal glycol groups.

Shen and Owens [14], working in our laboratories, observed an interesting maximum in the viscosity of water-soluble dextran-g-acrylamide copolymers prepared under varying Ce(IV) concentrations. Development of new characterization techniques including aqueous size exclusion chromatography have made possible extension of this initial work.

Most previous acrylamide-grafted polysaccharides reported in the literature were prepared under heterogeneous reaction conditions precluding careful control of the number and distribution of grafting sites along the polysaccharide backbone. Characterization has been difficult due to lack of complete solubility of the reactant polysaccharide or product graft copolymers.

EXPERIMENTAL

Materials

Acrylamide (AM) was obtained from Eastman Kodak and recrystallized twice from acetone prior to use. Dextran (T-500, molecular weight 520,000) was obtained from Pharmacia Chemical Co. Amylose and amylopectin were obtained from ICN Pharmaceuticals. Ceric ammonium nitrate, reagent grade, from Mallinckrodt Chemical Co. was used without further purification. Enzyme DL-100 (Diazyme) was obtained from Miles Laboratories. Sodium periodate was obtained as reagent grade from Matheson, Coleman, and Bell.

Synthesis of Graft Copolymers

Dextran-g-acrylamide copolymers were synthesized under the carefully varied reaction conditions shown in Table 1. A description of a typical reaction follows. Into a 500 mL, 3-necked, round-bottomed flask equipped with mechanical stirrer, nitrogen inlet tube, rubber septum, and addition funnel was placed a solution of 1.25 g (0.0077 mol of anhydroglucose units) of dextran in 125 mL of distilled water. Acrylamide, 8.165 g (0.115 mol) was added in one portion. Nitrogen was bubbled through the solution for 30 min. Ten milliliters of a 0.05 $\underline{N}$ nitric acid solution containing 0.0274 g (0.05 mmol) of ceric ammonium nitrate was then injected. The reaction mixture was stirred for 3 h at 25°C under nitrogen. The resulting viscous solution was diluted with 2250 mL of distilled water and then precipitated in portions by addition to acetone. The resulting polymer was dissolved in water and reprecipitated from acetone twice. Conversion was calculated prior to further extraction or purification procedures:

$$\% \text{ conversion} = \frac{\text{wt of isolated polymer}}{\text{wt of dextran} + \text{wt of acrylamide}} \times 100$$

Purification of the Dextran-g-acrylamide Copolymers

The crude polymeric product from the copolymerization reaction was purified by fractional precipitation of the aqueous solutions with acetone. An anthrone reagent [8] and ultraviolet spectroscopy were used to quantitatively follow the polysaccharide content in the dilute phase during precipitation. With this method as previously described [2], it is possible to separate the graft copolymer from unreacted dextran and homopolyacrylamide.

TABLE 1. Reaction Parameters for the Preparation of Dextran-g-acrylamides

Sample	Reaction time (h)	AM concentration (mmol)	Dextran[a] concentration (mmol)	Ce(IV) concentration (mmol)	Reaction temperature (0°C)	HNO_3 concentration (mmol)	Conversion (%)
AD-T1	0.5	115	7.7	0.050	25	0.50	69.8
AD-T2	1.0	115	7.7	0.050	25	0.50	76.4
AD-T3	1.5	115	7.7	0.050	25	0.50	78.8
AD-T4	2.0	115	7.7	0.050	25	0.50	86.7
AD-T5	2.5	115	7.7	0.050	25	0.50	88.3
AD-T6	3.0	115	7.7	0.050	25	0.50	93.5
AD-T7	3.5	115	7.7	0.050	25	0.50	97.4
AD-A1	3.0	230	7.7	0.050	25	0.50	49.2
AD-A2	3.0	173	7.7	0.050	25	0.50	68.5
AD-A3	3.0	115	7.7	0.050	25	0.50	93.5
AD-A4	3.0	86	7.7	0.050	25	0.50	72.7
AD-A5	3.0	58	7.7	0.050	25	0.50	45.9
AD-A6	3.0	29	7.7	0.050	25	0.50	33.0
AD-D1	3.0	115	23.1	0.050	25	0.50	97.2
AD-D2	3.0	115	15.4	0.050	25	0.50	95.4
AD-D3	3.0	115	11.6	0.050	25	0.50	93.8
AD-D4	3.0	115	7.7	0.050	25	0.50	93.5
AD-C1	3.0	115	7.7	0.005	25	0.50	76.4
AD-C2	3.0	115	7.7	0.010	25	0.50	85.9
AD-C3	3.0	115	7.7	0.025	25	0.50	89.2
AD-C4	3.0	115	7.7	0.035	25	0.50	91.1
AD-C5	3.0	115	7.7	0.050	25	0.50	93.5

AD-C6	3.0	115	7.7	0.065	25	0.50	93.8
AD-C7	3.0	115	7.7	0.075	25	0.50	94.6
AD-C8	3.0	115	7.7	0.100	25	0.50	95.9
AD-C9	3.0	115	7.7	0.500	25	0.50	97.3
AD-H1	3.0	115	7.7	0.050	25	0.25	81.2
AD-H2	3.0	115	7.7	0.050	25	0.50	93.5
AD-H3	3.0	115	7.7	0.050	25	1.00	71.4
AD-M1	3.0	115	7.7	0.050	25	0.50	93.5
AD-M2	3.0	115	7.7	0.050	25	0.50	93.3
AD-M3	3.0	115	7.7	0.050	40	0.50	93.0
AD-M4	3.0	115	7.7	0.050	50	0.50	92.7

[a] Dextran ($\overline{M}_w$ = 340,000) concentration is based on millimoles of AGU repeating units.

TABLE 2. Polysaccharide-g-acrylamide Copolymers Prepared by Reacting 0.0077 mol of Substrate with 0.115 mol of Acrylamide and 10 mL of 0.05 M HNO_3 at 25°C for 3 h

Sample	Substrate	$\overline{M}_w$[a]	Ce(IV) conc. (mmol)	Nitrogen[b] content (%)	Elemental analysis			[η] at 30°C (dL/g)
					C%	H%	N%	
AD3-1	Dextran	15,000-20,000	0.025	14.05				2.04
AD3-2	"	"	0.050	14.48	44.03	7.56	14.80	2.98
AD3-3	"	"	0.075	14.53				2.50
AD3-4	"	"	0.100	14.66				2.35
AD7-1	"	37,000-43,000	0.025	14.13				2.47
AD7-2	"	"	0.050	14.68	45.01	7.58	14.91	3.63
AD7-3	"	"	0.075	14.84				2.75
AD7-4	"	"	0.100	14.95				2.59
AD12-1	"	100,000-200,000	0.025	14.72				3.34
AD12-2	"	"	0.050	14.93	45.83	7.22	15.08	4.12
AD12-3	"	"	0.075	14.98				3.76
AD12-4	"	"	0.100	15.06				3.57
AD17-1	"	200,000-300,000	0.025	14.84				3.42
AD17-2	"	"	0.050	15.23	45.33	7.60	15.35	4.65
AD17-3	"	"	0.075	15.31				3.86
AD17-4	"	"	0.100	15.40				3.61

AD20-1	"	5-40 million	0.025	13.85				7.88
AD20-2	"	"	0.050	14.02	44.88	7.63	14.26	5.73
AD20-3	"	"	0.075	14.11				4.19
AD20-4	"	"	0.100	14.23				3.27
AP3-1	Amylopectin	>150,000	0.025	13.70				5.00
AP3-2	"	"	0.050	14.20	45.30	7.55	15.35	7.26
AP3-3	"	"	0.075	14.27				5.39
AP3-4	"	"	0.100	14.52				3.73
AY3-1	Amylose	>150,000	0.025	13.56				3.52
AY3-2	"	"	0.050	14.01	44.12	7.64	15.92	4.75
AY3-3	"	"	0.075	14.22				4.25
AY3-4	"	"	0.100	14.34				3.09

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[a] Supplied by manufacturer from light-scattering data.
[b] Micro-Kjeldahl analysis.

Size Exclusion Chromatography

Aqueous size exclusion chromatography (SEC) with a Waters Associates Liquid Chromatograph ALC 300 with a Model R-401 Refractometer was utilized to monitor hydrodynamic volume for the purified graft copolymers prepared under controlled reaction conditions.

The column set utilized in this work consisted of 14 columns (0.76 cm i.d. and 60 cm in length) packed with porous glass beads (4 of 10,000 Å, 4 of 3000 Å, 3 of 250 Å pore size) and silica (3 with 25,000 Å pore size). These columns were thermostatically controlled at 25 ± 1°C. Each sample (0.05 g/dL, 1 cc) was injected through the injection loop. The pressure was maintained at less than 2000 psi and the flow rate at 2 mL/min. Deionized water with 1% morpholine was used as the elution solvent.

Nitrogen Analysis

The nitrogen content of each graft copolymer was determined by elemental analysis (Galbraith Laboratories) or by micro-Kjeldahl analysis (Table 2).

Determination of the Number of Grafting Sites and Side-Chain Graft Length

Two methods were utilized to hydrolyze the polysaccharide backbone of the graft copolymers in order to determine the average graft lengths and the number of grafting sites—enzyme hydrolysis and periodate/NH_4OH hydrolysis.

In the enzyme hydrolysis method, the procedure was a slightly modified version described by Fanta et al. [15]. Into 100 mL of graft copolymer solution (2 g/dL), 1 mL of Diazyme DL-100 enzyme solution was added and stirred at 60°C for 24 h. The mixture was then heated at 95°C for 15 min to destroy the enzyme. After cooling, the solution was dialyzed against water and centrifuged to remove the insolubles. Polyacrylamide was isolated from the supernatant by freeze drying and the viscosity was measured in water at 25°C.

Number-average molecular weight, $\overline{M}_n$, and weight-average molecular weight, $\overline{M}_w$, were calculated from the following equations using experimentally determined intrinsic viscosities [15, 16]:

$$[\eta] = 6.8 \times 10^{-4} (\overline{M}_n)^{0.66}$$

$$[\eta] = 6.31 \times 10^{-5} (\overline{M}_w)^{0.80}$$

Periodate Hydrolysis

In this $NaIO_4/NH_4OH$ system, hydrolysis of the polysaccharide backbone was monitored with an anthrone reagent [8]. The absorbance, A, of the sample after hydrolysis was determined at 630 nm using ultraviolet spectrometry. To a 100-mL solution of graft copolymer (2 g/dL), 0.2 mL concentrated NH_4OH and 0.5 g of $NaIO_4$ were added. The reaction was conducted in the dark at 35° C for 1.5 h; the solution was then dialyzed against water and was freeze dried. Polyacrylamide weight fraction (W_{PAM}) in the copolymer can be calculated as follows:

$$\frac{\text{wt of polyacrylamide}}{\text{wt of graft polymer sample}} = W_{PAM}$$

The number of grafting sites can be calculated [17] from the average molecular weight of PAM side chain and W_{PAM} by

$$\text{number of grafting sites} = \frac{\overline{M}_w \text{ of graft copolymer} \times W_{PAM}}{\overline{M}_w \text{ of PAM side chain}}$$

The average molecular weight of the graft copolymer can be calculated from the average molecular weight of the dextran backbone and the weight fraction of polyacrylamide in the graft copolymer by

$$\frac{\overline{M}_w \text{ of graft copolymer}}{\overline{M}_w \text{ of dextran}} = \frac{1}{1 - W_{PAM}}$$

Viscosity Measurements

Cannon-Fenske capillary viscometers were used to measure relative, reduced, and intrinsic viscosities (Table 2) of the various polymer solutions. Intrinsic viscosities were obtained by extrapolation of both reduced viscosities, η_{sp}/C, and inherent viscosities, $\ln \eta_r/C$, to infinite dilution. Capillary sizes were chosen for the best compromise of solvent and solution flow times for the range of polymer concentrations from 0.3 to 0.1 g/dL.

A four-bulb shear rate viscometer (Cannon-Ubbelohde Co.) which gave a shear range of 50 to 1500 s^{-1} was used to measure the pseudoplastic behavior of the graft copolymers [18, 19]. All measurements were conducted after the same time interval (7 d) from solution (0.2

g/dL) preparation to minimize the aging effect. The shear rate constant K of each bulb given by the manufacturer was: Bulb 1, 125,000; Bulb 2, 64,000; Bulb 3, 26,500; and Bulb 4, 12,000 s^{-1}. Shear rate (D) was calculated by the following equation where t is the efflux time of polymer solution [18-22]:

$$D = K/t \ (s^{-1})$$

RESULTS AND DISCUSSION

Synthesis and Purification

Synthetic conditions (Table 1) were systematically varied in order to assess the influence of each reaction parameter on the hydrodynamic volume of the resulting dextran-g-acrylamide copolymers. Thus five series of reactions were conducted in which one reaction condition [time, acrylamide concentration, dextran concentration, Ce(IV) concentration, reaction temperature, or nitric acid concentration] was varied while keeping the other conditions constant.

The product graft copolymers were purified as described in the experimental section by fractional precipitation using acetone as a nonsolvent. With Ce(IV)/HNO_3-induced initiation under the conditions listed in Table 1, little homopolymer was detected. Our previous work [2] with the Fe(II)/H_2O_2 initiation system demonstrated homopolyacrylamide formation even under carefully optimized conditions.

Evidence for only minor quantities of homopolyacrylamide in the reaction products was substantial. For example, for Sample AD-C5 little change was noted in the polysaccharide content of the dilute phase monitored by ultraviolet spectrometry of the anthrone complex. Intrinsic viscosities and elemental analyses of the purified copolymer and the crude reaction product were very close in value. Only a slight change in shape of the size exclusion chromatogram was noted after purification; the elution volumes were identical for the crude Product AD-C5 and the purified Product AD-C5A (Fig. 1). These slight changes can be attributed to small changes in total composition of the copolymer due to incomplete removal of the low molecular weight fractions from solution during precipitation.

Effects of Reaction Parameters on Graft-Copolymer Hydrodynamic Volume, Conversion

Increased reaction times for the AD-T series (Table 1), as expected, increased both conversion and hydrodynamic volume as measured by size exclusion chromatography.

A maximum in conversion was observed for Sample AD-A3 in which the concentration was 0.155 mol (Fig. 2). Hydrodynamic volumes for

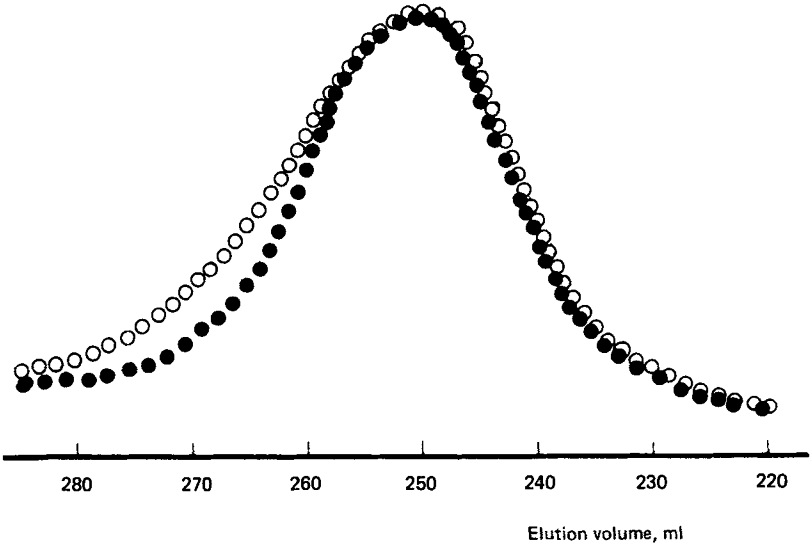

FIG. 1. Size exclusion chromatogram of the crude reaction Product AD-C5 (○) and the purified Product AD-C5A (●).

the AD-A series could not be compared since all copolymers eluted at the void volume for the column set used.

Increasing dextran concentration for the AD-A series resulted in a slight increase in conversion as well as an increase in SEC elution volume (lower hydrodynamic volume). A broadening of the chromatogram with increased dextran concentration was also observed.

The effects of temperature and nitric acid concentration on elution volume were negligible over the range studied. Conversion was approximately 93% for the AD-M series; the highest conversion for the AD-H series occurred at 5.0×10^{-4} mol of HNO_3.

The effect of Ce(IV) concentration on hydrodynamic volume and conversion was significant over the range from 5.0×10^{-5} to 5.0×10^{-4} mol. Conversion steadily increased with increasing Ce(IV) concentration. The SEC chromatograms (Fig. 3) indicated that the hydrodynamic volumes of the graft copolymers decreased in the following order: AD-C6 > AD-C5 > AD-C8 > AD-C1 > AD-C9 representing Ce(IV) concentrations of 0.065, 0.050, 0.100, 0.005, and 0.500 mmol, respectively. A maximum in hydrodynamic volume for this series appeared at 0.065 mmol of Ce(IV).

Similar effects of Ce(IV) concentration in intrinsic viscosity were observed (Fig. 4) for the acrylamide-grafted dextran, amylose (Fig. 5), and amylopectin copolymers (Fig. 6). Interestingly, a maximum in intrinsic viscosity was observed for copolymers prepared from several molecular weight ranges of dextran and for the highly branched amylopectin as well as linear amylose.

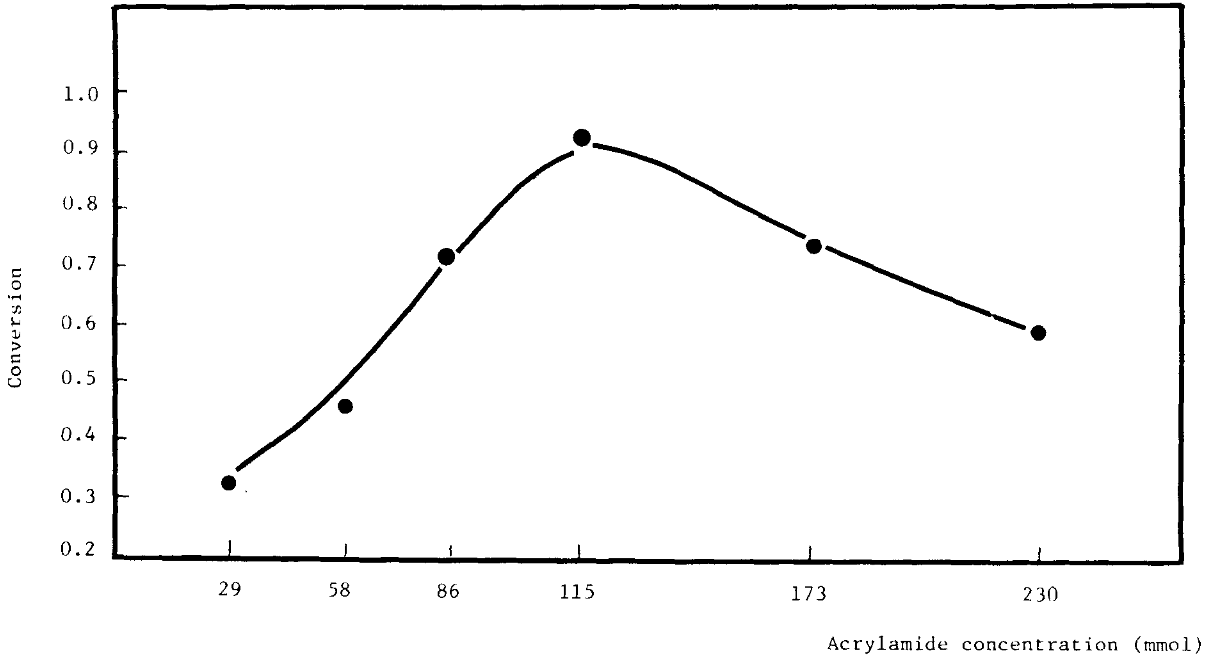

FIG. 2. Effects of monomer concentration on conversion for series AD-A (Table 1).

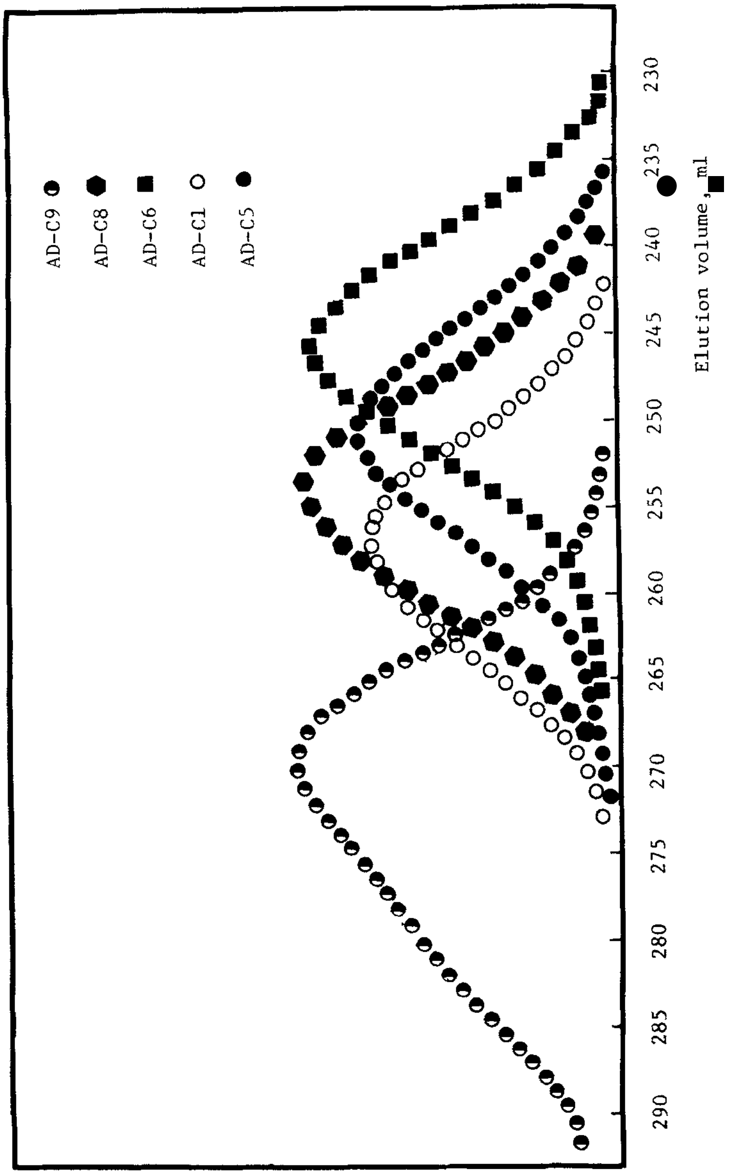

FIG. 3. Representative SEC curves of dextran-g-acrylamides, Series AD-C (Table 1) prepared at varying Ce(IV) concentrations.

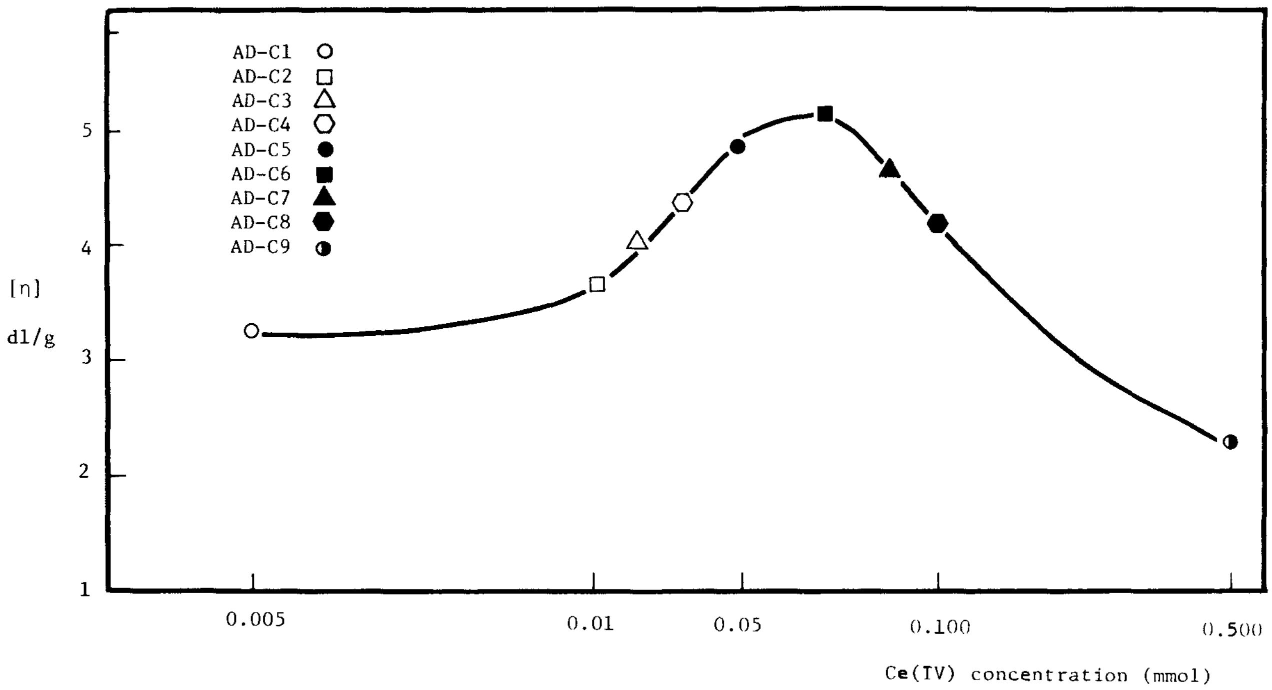

FIG. 4. Effects of Ce(IV) concentration on viscosity in water at 30°C of dextran-g-acrylamides AD-C series (Table 1).

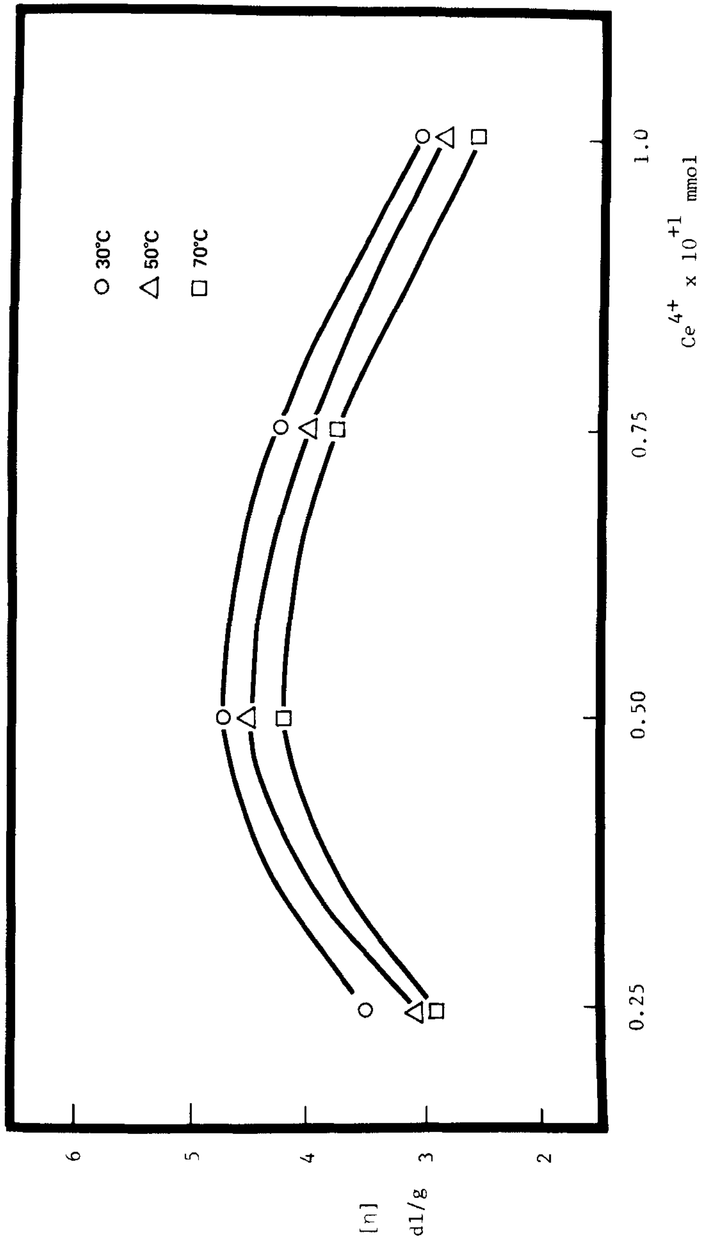

FIG. 5. Effect of Ce(IV) concentration on viscosity of amylose-g-acrylamides, Series AY3 (Table 2) in water.

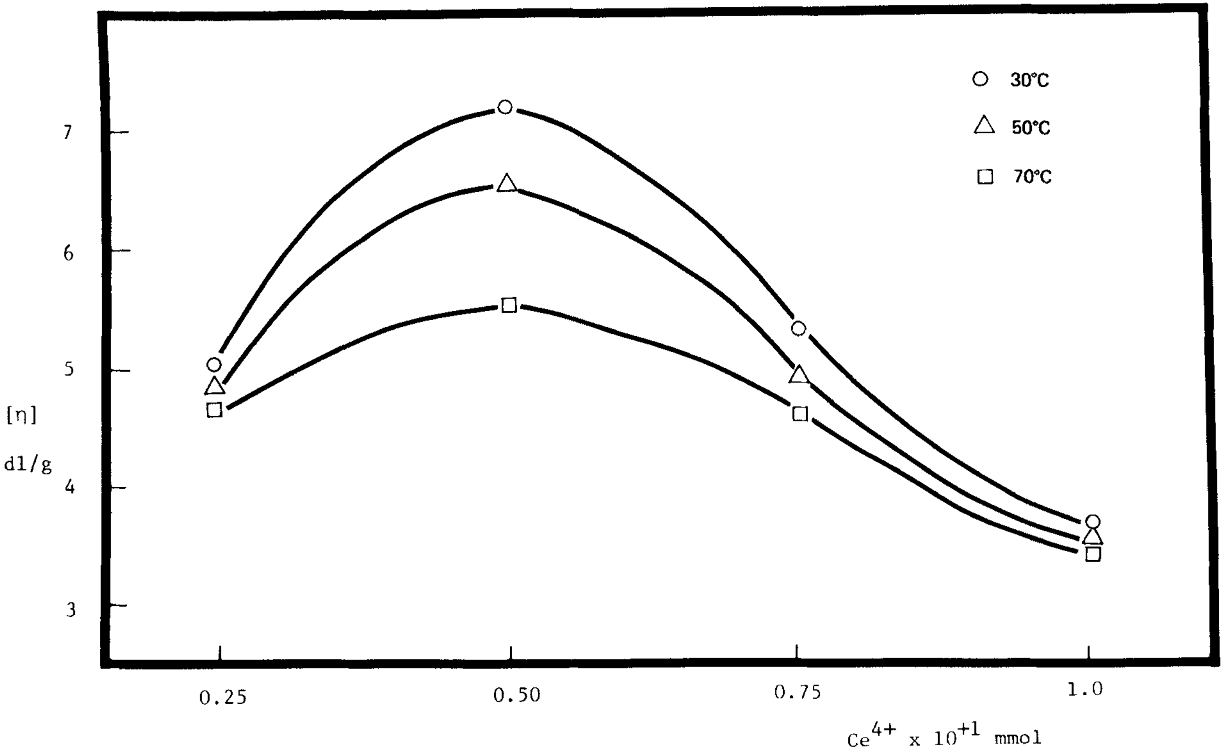

FIG. 6. Effect of Ce(IV) concentration on viscosity of amylopectin-g-acrylamides, Series AP3 (Table 2) in water.

The only sample showing deviation from this trend was AD20-1 prepared from dextran of $\overline{M}_w$ = 5 to 40 million.

Structural Determination

To assess if these maxima in hydrodynamic volume at specific Ce(IV) concentrations are related to average number of grafting sites, length of polyacrylamide grafts, and/or total molecular weight, Series AD-C (Table 1) was subjected to enzymatic (Diazyme DL-100) and periodate/NH_4OH hydrolysis. After hydrolysis of the polysaccharide backbone, the residual polyacrylamide was isolated and its molecular weight determined by viscosity. From the nitrogen analysis and the molecular weight of the dextran, the number of grafting sites and the molecular weight of the graft copolymer were calculated as described in the experimental section.

A comparison of the two hydrolysis methods is shown in Table 3. The percent hydrolysis of the dextran was measured spectroscopically utilizing the anthrone reagent [8]. Only 60-90% of the dextran backbone was hydrolyzed using the enzyme method whereas 85-90% hydrolysis was obtained with $NaIO_4/NH_4OH$.

The calculated values of molecular weight for the latter method are obviously more accurate. However, these values are probably higher than the actual values due to the remaining polysaccharide residues. (Hydrodynamic dimensions would be only slightly affected since water is a poor solvent for dextran and a good solvent for polyacrylamide.)

Table 4 summarizes the data calculated for AD-C1 through AD-C9. AD-C6, which showed the highest intrinsic viscosity (Fig. 4) and the highest hydrodynamic volume (Fig. 3), has the lowest number of grafting sites (1.85), the highest molecular weight of the side-chain graft (630,000), and the highest total molecular weight (1,690,000). A sample by sample comparison clearly shows a one-to-one correspondence between hydrodynamic volume (as measured by viscosity and SEC) and molecular weight of the polyacrylamide side chain. Total molecular weight of the graft copolymer does not correspond as well as shown by comparison of Samples AD-C8, AD-C3, and AD-C4.

The shear rate dependent viscosities of the dextran-g-acrylamide copolymers are shown in Fig. 7. The order and magnitude of the relative viscosities as well as the pseudoplastic behavior illustrate the importance of the acrylamide side chain on hydrodynamic behavior.

CONCLUSIONS

It may be concluded that side-chain graft length and number of grafting sites greatly affect macromolecular dimensions of dextran-g-acrylamide copolymers. Under the synthetic conditions employed

TABLE 3. Hydrolysis Data on Effects on Variation of Ce(IV) Concentration on the Grafting of Dextran with Polyacrylamide

Sample	% Nitrogen	$\overline{M}_W$ of graft polymer	$\overline{M}_W$ of PAM graft	Number of graft sites	% PAM	Absorbance	% Hydrolysis
			Enzyme Hydrolysis				
AD-C3	14.82	1,960,000	598,000	2.45	74.9	0.17	69
AD-C5	15.08	2,100,000	731,000	2.16	75.2	0.18	67
AD-C7	15.15	2,070,000	650,000	2.43	76.4	0.20	64
AD-C8	15.18	1,890,000	615,000	2.39	77.6	0.22	60
			Periodate Hydrolysis				
AD-C3	14.82	1,620,000	476,000	2.31	68.0	0.053	90
AD-C5	15.08	1,670,000	601,000	1.91	68.9	0.052	91
AD-C7	15.15	1,650,000	487,000	2.37	70.0	0.065	88
AD-C8	15.18	1,630,000	471,000	2.48	71.0	0.084	85

TABLE 4. Effects of Variation Ce(IV) Concentration on the Resulting Dextran-g-acrylamide Structures

Sample	mmol	% Nitrogen	$\overline{M}_w$ of PAM graft	$\overline{M}_w$ of graft polymer	Number of graft sites	$[\eta]$ at 30° C
AD-C1	0.005	14.03	463,000	1,580,000	2.29	3.21
AD-C2	0.010	14.72	468,000	1,610,000	2.19	3.64
AD-C3	0.025	14.82	476,000	1,620,000	2.31	4.31
AD-C4	0.035	14.98	482,000	1,630,000	2.31	4.72
AD-C5	0.050	15.08	601,000	1,670,000	1.91	4.86
AD-C6	0.065	15.13	630,000	1,690,000	1.85	5.12
AD-C7	0.075	15.15	487,000	1,650,000	2.37	4.57
AD-C8	0.100	15.18	471,000	1,630,000	2.48	4.08
AD-C9	0.500	15.68	340,000	1,520,000	3.24	2.28

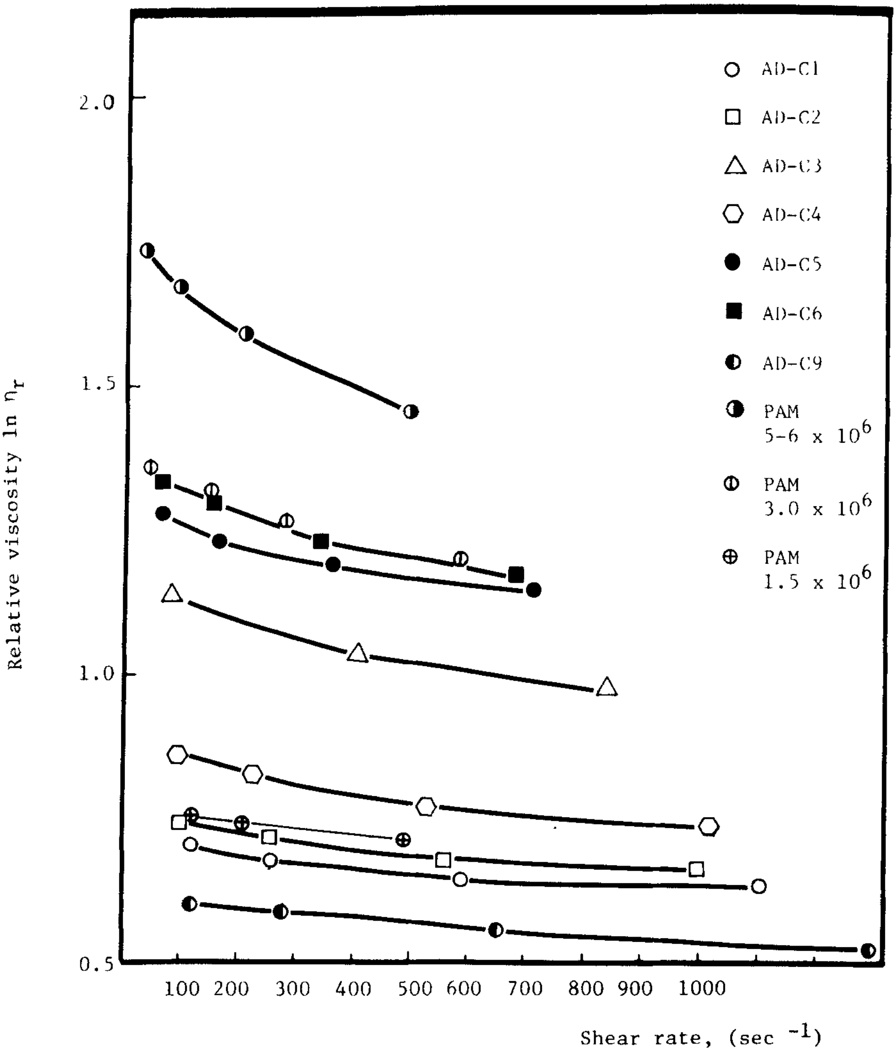

FIG. 7. Shear rate dependence of viscosity for dextran-g-acrylamides, Series AD-C (Table 4) in water at 30°C at a concentration of 0.2 g/dL.

in this study, a clear relationship exists between hydrodynamic dimensions, as measured by viscosity and size exclusion chromatography, and molecular weight of the side-chain grafts. Significant increases in solution dimensions over ungrafted dextran were obtained. The maximum observed in the hydrodynamic volume as a function of Ce(IV) concentration in the reaction mixture is reproducible by both SEC and viscosity measurements. It is clear that fewer numbers of long-chain polyacrylamide grafts result in larger hydrodynamic dimensions than a large number of short-chain grafts. For AD-C9, prepared with the highest Ce(IV) concentration, the nitrogen content was highest (15.68%) and the viscosity lowest (2.28 dL/g) with 3.2 polyacrylamide chains. In AD-6 the frequency of grafting was lower (1.9) as was the nitrogen content (15.13%), but the viscosity was highest (5.12) and the polyacrylamide chains the longest ($\overline{M}_w$ = 630,000) in the series.

The lack of correspondence between the number of grafting sites per molecule and the initial Ce(IV) concentration in the reaction mixture is puzzling. Site selectivity or a concentration dependency on the rates of complex formation and/or disproportionation are possible explanations. Certainly these effects need further elucidation.

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